

NaphthaMax[®] III: Flexibility and Value in Challenging Economic Times

Executive Summary

Refiners the world over are focused on optimizing their operations and employing Fluid Catalytic Cracking (FCC) solutions that help maximize margins. Lower refinery utilization numbers due to current global pressures are challenging refiners' earnings. Given these conditions and the pressures put on the FCC unit, flexibility in operation will be key for refiners looking to capture market opportunities and regain healthy margins. NaphthaMax[®] III, the latest evolution from BASF's award-winning Distributed Matrix Structures (DMS) technology platform, sets a new standard for performance in the current FCC operating environment. NaphthaMax III has the commercially-proven ability to provide high bottoms conversion with low delta coke and higher yields of valued gasoline and light olefin products compared to other existing technologies.

In line with BASF's commitment to accelerating innovation in support of the FCC market, an R&D project was initiated to focus on optimizing the manufacturing and performance of DMS-based products. The results of this research and development work led to a \$30MM investment to drive targeted improvements in product quality and manufacturing process consistency. This investment enabled an improvement in quality and efficiency achieved through upgrades of commercial calcination and rare earth exchange operations. NaphthaMax III is the direct result of the implementation of these efforts, bringing to market a highly coke-selective catalyst that delivers improved FCC performance.

The initial demonstration of this technology was undertaken at Marathon

Petroleum's Garyville, LA, refinery in late 2008 after successful pilot plant testing in the circulating riser pilot plant at Marathon's Catlettsburg, KY R&D facility. This was a back-to-back trial with NaphthaMax II giving a perfect opportunity for a commercial comparison with the leading gasoil max conversion product on the market. The pilot plant work conducted by Marathon demonstrated the superior coke selectivity and gasoline yields for NaphthaMax III, and the commercial results confirmed the pilot plant findings. At constant conditions, regenerator temperature dropped by ~20°F. The regenerator temperature decline allowed the unit circulation to "wind up" resulting in higher conversion and greater gasoline and liquid petroleum gas (LPG) yields. Slurry yield declined by 1 volume percent. The projected economic benefit based on pilot plant testing was \$0.68/bbl. The actual value determined from a post-audit performance review was \$0.71/bbl allowing the unit to meet its processing objectives.

DMS Technology Platform

BASF's innovative DMS technology revolutionized the FCC market with the introduction of NaphthaMax in 2000. The DMS technology platform was truly an innovative milestone in the industry, providing catalyst with unique catalyst pore architecture and optimized porosity for heavy feed molecule diffusion. The catalyst's selective zeolite-based cracking additionally provides excellent deep bottoms conversion with unrivaled

coke selectivity. Since its commercial introduction, the NaphthaMax family of products has demonstrated successful operation in over 140 commercial FCC applications. With their unparalleled commercial performance, DMS technology platform products have enjoyed rapid and successful acceptance by users looking for high conversion, maximum total liquid and coke selective FCC catalyst products.

NaphthaMax was the first catalyst based on the DMS platform, as well as the first FCC catalyst developed specifically to address the needs of short contact time (SCT) process designs. In these advanced designs, the combination of higher catalyst activity along with typically higher reaction temperatures and shorter contact times, all contribute to increasing the importance of diffusion in the FCC catalyst. The structure imparted by the novel DMS matrix is designed to provide enhanced diffusion of the feed molecules to pre-cracking sites located on the external, exposed surface of highly dispersed zeolite crystals. The feed initially cracks on the zeolite surface itself, rather than on an active amorphous matrix material, as is the case with other FCC catalyst technologies. This difference results in improved selectivities, with reduced coke formation, characteristic of zeolite cracking. The secondary diffusion pathway of the cracked products to the internal crystalline zeolite surface is also minimized, resulting in less overcracking. The net commercial result is high bottoms conversion with low delta coke, and higher yields of valued gasoline and light olefin products.

This unique structure of the DMS technology is illustrated in the SEM micrograph of the interior of a catalyst particle shown in Figure 1. The well-developed pore structure is evident, and essentially the entire exposed pore surface is covered with zeolite crystallites. The external surfaces of these crystallites are exposed and accessible to the hydrocarbon feed molecules, which diffuse readily through the open pore architecture. While other catalyst technologies may feature similar or even higher total pore volumes, they do not have the same morphology and inherent zeolite-based cracking pattern imparted by the DMS structure.

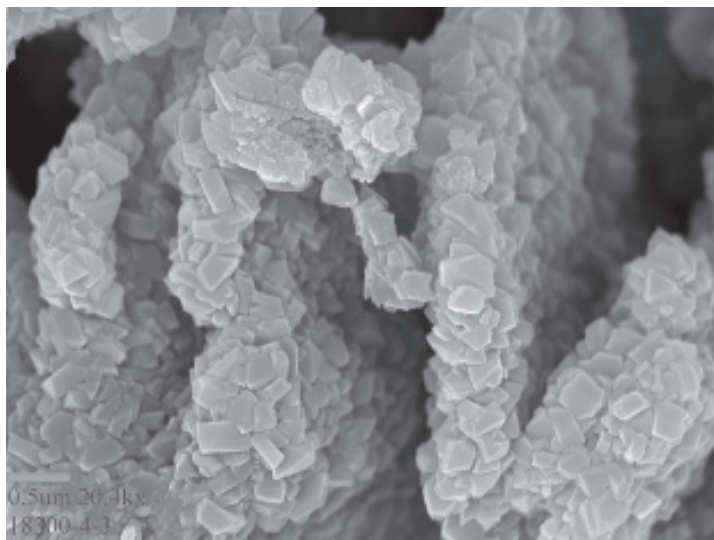


Figure 1: SEM micrograph of interior of DMS-based catalyst particle

BASF's *in situ* FCC Technology

BASF's unique and patented technology for FCC catalyst manufacture delivers FCC catalysts with unique physical attributes that provide refiners with high yield, coke selective, robust FCC catalyst technology. The process involves crystallizing Y zeolite "*in situ*" inside of pre-formed microspheres. The key raw material in the process is specially selected kaolin clay (aluminum silicate), which is mined and processed in BASF's Middle Georgia operations. After mining, the kaolin clay undergoes a series of refining and conditioning steps in preparation for further manufacturing and tailoring for specific catalytic features.

In the manufacturing of the microspheres, the feed components (kaolin clay, active ingredients and binder) for microsphere formulation are combined into slurry and spray dried. The spray dried particles (microspheres) are then transferred into rotary calciners, where they are treated at temperatures of up to 1800°F prior to zeolite crystallization.

This high temperature calcination step gives catalyst produced by the *in situ* method the key advantage of a stable, attrition resistant matrix. The physical properties given to the microsphere at this stage of the process are relatively unchanged as the catalyst is exposed to the lower temperature environment of the FCC regenerator. Given the sensitivity of zeolite to high temperatures, this calcination step is a critical difference with competing incorporated manufacturing, where the zeolite is blended and spray dried with the other components prior to the calcination step.

The finished microspheres are then reacted with silicates and other nutrients along with zeolite precursors or seeds to promote the growth of the actual zeolite crystals. In specific, the microspheres are treated with caustic to leach silica from the particle, thus forming a network of pore channels along which the zeolite crystals are grown *in situ*. This unique procedure results in complete dispersion of zeolite crystals along the pore walls on the alumina rich matrix. Growth of the zeolite within the microsphere pore structures yields a high degree of interaction between the zeolite and matrix surfaces forming intense chemical bonds. Attrition resistance of the particle actually increases following the zeolite crystallization step.

The matrix zeolite bond stabilizes the zeolite and makes it extremely resistant to sintering or pore collapse, yielding unparalleled hydrothermal stability. The crystallization process

conditions can be varied over a wide range of conditions to yield specific catalyst properties, such as in the case of DMS, providing maximum exposure of the active zeolite.

In a series of ion exchanges with ammonium and rare earth cations and drying and calcination steps, the crystallized products are subsequently converted into a low sodium catalyst with high hydrothermal stability. BASF has made tremendous strides in developing catalyst technologies that offer the lowest sodium levels in industry, as it is well known that Na cations have a negative impact on zeolite stability.¹ Na cations in the presence of steam are converted to sodium hydroxide. Sodium hydroxide catalyzes the hydrolysis of the Si-OH bonds leading to zeolite collapse.

The BASF *in situ* crystallization technology allows for the creation of active zeolite and matrix functionalities in the accessible regions of the microsphere. All zeolite and matrix sites are located in areas of the catalyst that are able to efficiently come in contact with the FCC feed molecules (Figure 2). This represents a profound advantage over competitive processes that use separately made zeolite and matrix components and create the final catalyst by mixing these together with a binder to produce the feed in a spray drying step. The binder in competitive technologies acts as a boundary layer and prevents an efficient interaction of the incorporated matrix and zeolite functionalities. Additionally, some of the active ingredients are made inaccessible to the

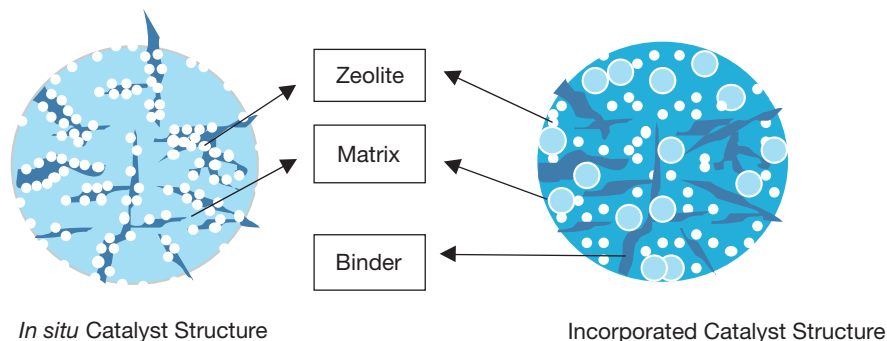


Figure 2: Representation of in situ and incorporated catalyst structures

feed molecules, thereby lowering their efficiency, or agglomerate, to form larger particles that promote undesirable secondary reactions, such as condensation to coke.

DMS Manufacturing Development

Keeping with BASF's drive for innovation and technology excellence, a process optimization initiative was undertaken by the FCC catalyst and additives manufacturing sites involving cross functional experts from BASF's Centers of Excellence in Ludwigshafen, Germany and the USA. The goal of this endeavor was to optimize the physical properties of BASF's DMS technology platform products as well as to increase efficiency and output from the manufacturing sites. This effort included all production processes starting from raw material acquisition through finished product manufacturing. Under the program umbrella, each key sub-process was manned by a team composed of engineers, manufacturing personnel, and research & development scientists. With the aid of sophisticated computer modeling techniques, areas of improvement were identified for the key process stages of calcination and ion exchange.

Calcination

Many of the processes associated with the manufacturing of BASF FCC products involve thermal treatment or calcination of reactive components and in-process catalyst materials. Through the calcination process, the FCC catalyst is

hydrothermally stabilized via reduction of its unit cell size. It is critical that this process be done under stable controlled conditions to avoid damage to the catalyst due to temperature gradients and fluctuations. Through thermal imaging and mathematical modeling of the calciner equipment, modifications for more efficient heat transfer were identified to ensure uniform thermal treatment under less severe conditions. These modifications allowed for increased throughput and more uniform heat distribution; thus eliminating the possibility of thermal degradation caused by extreme heat gradients.

The streamline plots in Figure 3 were generated using advanced thermal imaging and modeling techniques to illustrate the heat distribution across the calciners at the BASF manufacturing sites. The blue regions present in variations 0 and A represent cooler regions that created unwanted temperature gradients in the process. In variation B, the blue areas have been eliminated and more uniform heat distribution has been achieved through improvements in calciner burner arrangement and stack venting dynamics. These improvements resulted in more uniform temperatures throughout the calciner, thus minimizing thermal degradation of the zeolite. The second set of thermal images shows the increase in residence time at controlled temperature achieved through the optimization of the calciner equipment (Figure 4). As can be seen from the graphics, the bright red region increased significantly from variation 0 to B illustrating the longer residence time at the desired temperature range.

Results Comparison of Streamlines for Temperature

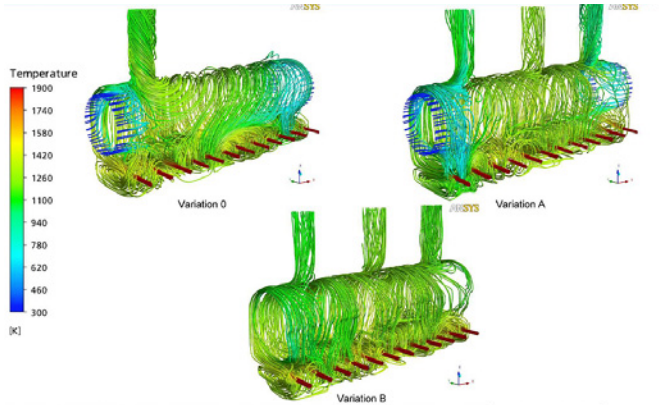


Figure 3: Streamline Plots for Calciner Temperature Flow

The optimization of the calciner resulted in longer residence time and more uniform exposure at target temperature, translating to an improvement in zeolite quality and stability.

Rare Earth (RE) Exchange

Rare earth oxides (REO) are key components in FCC catalysts as they add stability to the zeolite component and control catalytic selectivity during the cracking process. Achieving uniform distribution of the RE on catalyst particles at high or low REO levels is critical to catalyst performance. Through a detailed development program, the manufacturing process at BASF's manufacturing sites was modified to achieve optimal rare earth distribution. The objective was to minimize variations of the levels of REO over individual catalyst particles. This improvement in RE distribution directly improves catalyst performance by further eliminating variations in unit cell size and ensuring the ability to control the degree of hydrogen transfer reactions in the FCC unit.

New manufacturing procedures were implemented to further tighten the specifications on RE distribution across the catalyst production process. Figure 5 shows the RE gradient across

Results Comparison of Temperature at Retort Outer Wall (Top View)

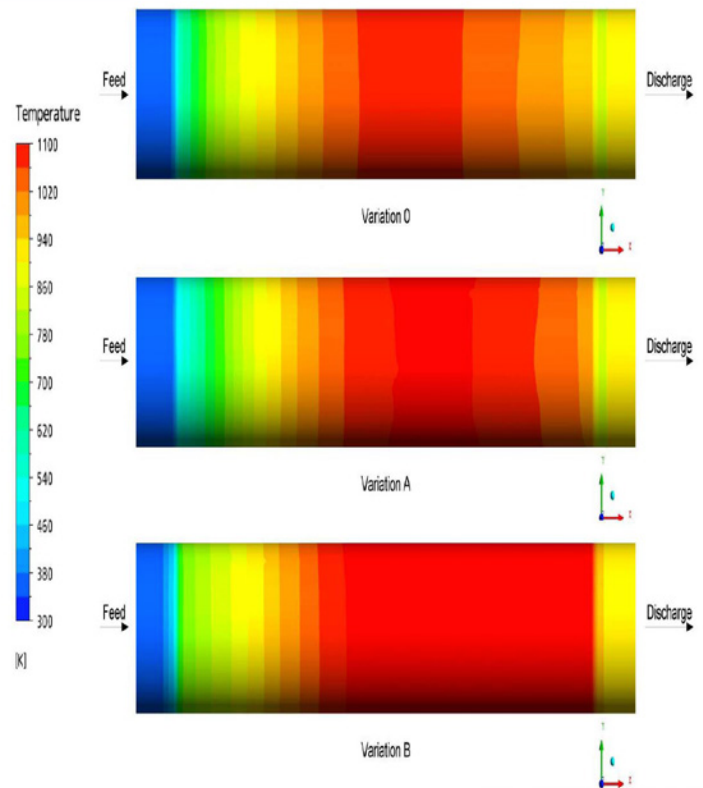


Figure 4: Thermal Imaging of Calciner

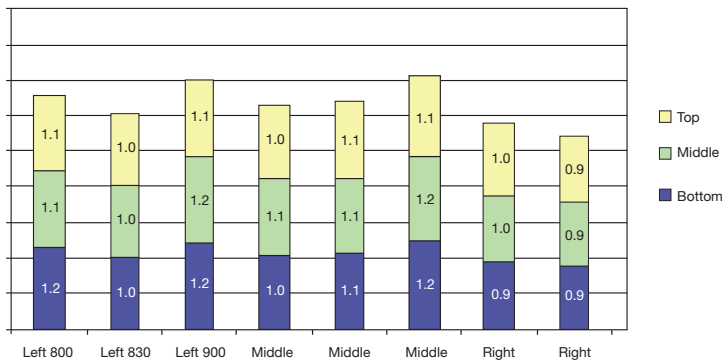


Figure 5: REO Distribution across Production Belt

the depth and width of a catalyst sample taken from one of the belt filters downstream of the rare earth exchange process.

The collective result of these improvements in manufacturing procedure resulted in the introduction of NaphthaMax III. The initial evidence of the improvement was seen by an increase in hydrothermal stability of the finished catalyst as shown in Table 1.

Positive Yield Shifts with NaphthaMax III		
	Previous Process	Improved Process
Percent TSA Retention	52 %	60 %
Percent ZSA Retention	49 %	56 %

Table 1: Hydrothermal stability data

Catalytic evaluation in an advanced cracking evaluation (ACE) laboratory test unit showed improved selectivity for NaphthaMax III versus the NaphthaMax II formulation. Compared to NaphthaMax II at the same zeolite and rare earth levels, NaphthaMax III yielded more gasoline and LPG with reduced light cycle oil (LCO) and bottoms at constant coke yield (Figure 6).

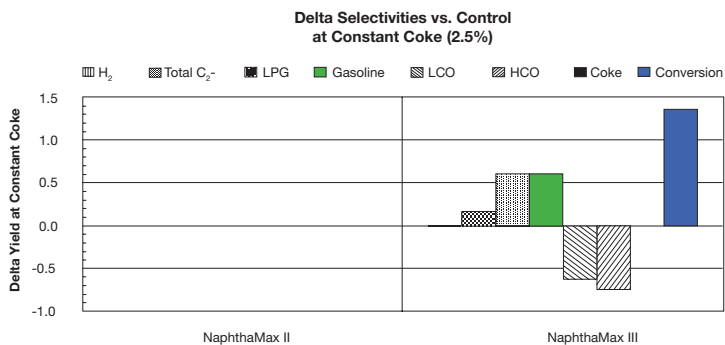


Figure 6: Incremental Yields for NaphthaMax III versus NaphthaMax II at Constant Coke

Marathon Refinery Trial Results

Marathon initiated a circulating pilot plant evaluation program based on the successful development of NaphthaMax III technology, which was the basis for considering further commercial trials in one of their six operating FCC units. Marathon FCC units have been regular users of NaphthaMax technology due to its good fit for Marathon's specific hardware, feedstock and operating conditions. Marathon's previous operating success and familiarity with the NaphthaMax product line provided a solid comparison base for the new NaphthaMax III catalyst.

After careful consideration, Marathon's Garyville refinery was selected for the commercial trial. This unit was using NaphthaMax II with a relatively low rare earth level of 1.4 wt% for about a year. With the use of NaphthaMax III, Marathon sought further improvements in coke selectivity to further reduce regenerator temperature while maintaining or improving gasoline selectivity.

NaphthaMax III was tested in Marathon's circulating riser FCC pilot plant at their Research & Development Center (RAD) in Catlettsburg, KY. Fresh samples of the current NaphthaMax II product in use at Garyville, along with commercially produced NaphthaMax III catalyst were steam deactivated by Marathon for 24 hours in 100% steam to match the equilibrium activity obtained in the Garyville FCCU. No metallation was performed on the catalysts prior to testing, as the Garyville unit typically

operates with low levels of metals contamination. An age distribution was also applied.

Marathon's RAD circulating pilot plant operates with the incumbent catalyst to best match the current unit performance. This commercial benchmark is an important part of the Marathon protocol. After potential catalyst systems are evaluated, an FCC process model uses catalyst factors and varies operating conditions and catalyst formulations to identify potential solutions for improved economic return on the commercial FCCU. In testing NaphthaMax III at RAD, Marathon found that NaphthaMax III gave improved performance over the incumbent NaphthaMax II.

Most important to Garyville was the further improvement in coke selectivity exhibited by NaphthaMax III vs. NaphthaMax II. As shown in Figure 7, NaphthaMax III consistently demonstrated improved coke selectivity over NaphthaMax II at various conversion levels. Commercially, this improvement in coke selectivity would be expected to translate to lower regenerator temperature, and high catalyst circulation, and thus higher conversion. In the pilot plant test, NaphthaMax III also exhibited better gasoline selectivity. In Figure 8, the gasoline selectivity is plotted against coke make to simulate the commercial impact expected in the actual FCCU.

Not surprisingly, the improved coke selectivity of NaphthaMax III also translated to lower dry gas make (Figure 9). As expected, no significant changes were observed in bottoms upgrading with the new formulation. LPG selectivities were only changed slightly with no definitive trend noted.

Based on the results of the pilot plant study, Garyville opted to make a change to the NaphthaMax III catalyst formulation. The change was initiated in August 2008. The Garyville FCCU is one of the largest cat crackers in North America. The feedstock is a combination of straight run vacuum gas oil (VGO), coker gas oils and deasphalted oil. Each of these streams is hydrotreated in front of the FCC. Purchased gas oils are also fed to the unit to supplement the available feed to the unit. The FCCU was originally designed as an Exxon Flexicracker in 1979, but has been modified through several revamps. The Garyville FCCU was utilizing a high activity

Garyville Fresh Catalyst Evaluation

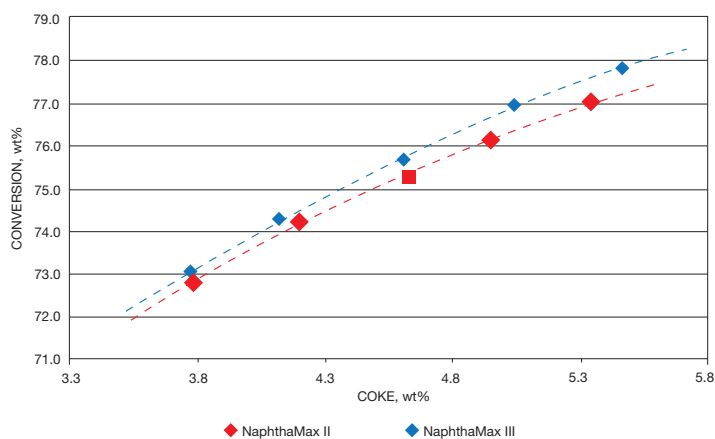


Figure 7: Improved Coke Selectivity of NaphthaMax III at Different Conversion Levels

Garyville Fresh Catalyst Evaluation

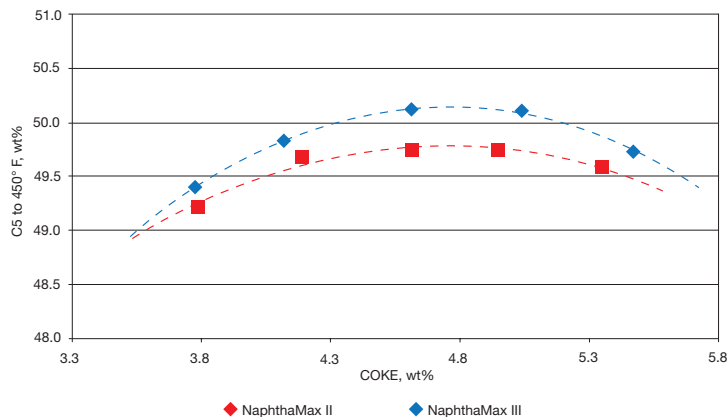


Figure 8: Gasoline Selectivity, NaphthaMax II vs. NaphthaMax III

Garyville Fresh Catalyst Evaluation

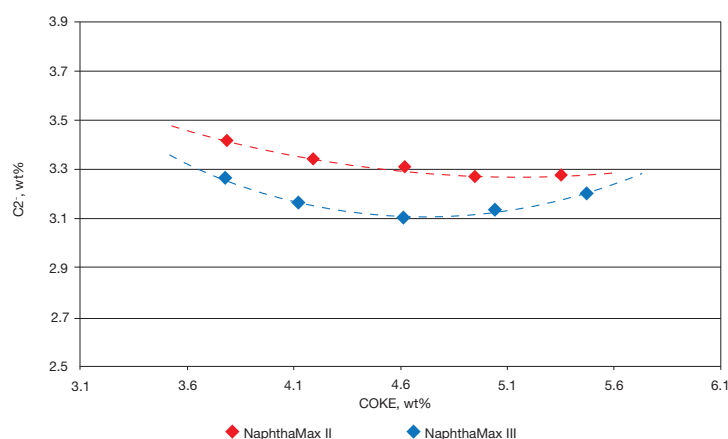


Figure 9: Dry Gas Yield NaphthaMax II vs. NaphthaMax III

NaphthaMax II formulation with 1.4 wt% rare earth when the decision was made to utilize NaphthaMax III. The projected benefits, based on the pilot plant and model optimization, were \$0.68/bbl.

Marathon conducted a post audit of the catalyst trial. Commercial data was normalized for feed quality and operating severity. Table 2 is a summary of the post audit results for NaphthaMax II and NaphthaMax III. As the table shows, during NaphthaMax III use, catalyst makeup rate was held essentially constant and equilibrium catalyst activity remained steady. Given the lower zeolite content of the fresh catalyst, this clearly illustrates the improved stability of NaphthaMax III. Meanwhile, feed quality declined a bit subsequent to the catalyst change. However, the decline is small and unlikely to have had a measureable impact on yields. The decrease in regenerator temperature and delta coke was driven by the improved coke selectivity of NaphthaMax III.

The yield shift experienced by the Garyville FCC resulted in significant value to the refinery. The commercial post audit identified \$0.71/bbl increased profitability. This is similar to the predicted value of \$0.68/bbl and validated the projected pilot plant economics and Marathon's protocol for catalyst selection.

Positive Yield Shifts with NaphthaMax III		
	Before	After
Feed Rate, BPD	BASE	+600
Feed API	BASE	-0.3
Feed Concarbon, wt%	BASE	-0.01
Feed UOP K	BASE	-0.10
Reactor Outlet Temp, °F	BASE	+3.6
Regenerator Bed Temp, °F	BASE	-19
Delta Coke, wt%	BASE	-0.05
Catalyst Addition Rate, tpd	BASE	-0.4
Ecat Activity, wt%	BASE	BASE
Normalized Yields (Feed & Severity)		
Conversion, vol %	BASE	+0.4
Gasoline, vol %	BASE	+1.3
Dry Gas, wt%	BASE	-0.6
Slurry, vol %	BASE	-0.6
Total Liquid, vol %	BASE	+0.4

Table 2: NaphthaMax II vs. NaphthaMax III Post Audit

Conclusion

Through collaboration of BASF's technical groups across Germany and the USA, manufacturing improvements were achieved that made the optimization of BASF's DMS-based products possible. The first product out to the market after completion of these upgrades is NaphthaMax III, a superior product that has been commercially demonstrated successfully at Marathon's Garyville refinery. The upgrades achieved in manufacturing led to direct improvements in the physical properties and in turn to the improved performance of the catalyst. The modifications not only allowed debottlenecking of specific assets, but also the marked improvements in prevention of thermal degradation during manufacturing and further tightening of the specifications on RE distribution across the catalyst production process.

The trial at Marathon's Garyville refinery was based on Marathon's pilot plant evaluation and was concluded in 2009. The unit experienced a decrease in regenerator temperature and delta coke due to the improved coke selectivity achieved with NaphthaMax III. This met the unit's processing objectives and allowed further unit optimization. As observed with other members of the NaphthaMax family of products, the award winning DMS technology platform delivered increased gasoline yield with a high degree of coke selectivity. NaphthaMax III showed extremely high hydrothermal stability, even at high severity operation. The commercial post audit identified \$0.71/bbl increased profitability. This is similar to the predicted value of \$0.68/bbl and validated the projected pilot plant economics and Marathon's protocol for catalyst selection. Due to the positive outcome of the trial, Marathon entered into a supply agreement for NaphthaMax III at the end of the trial. A total of four Marathon FCC units currently utilize NaphthaMax III.

References

1. M. Xu et al, J. Catal. 207, 237–246 (2002).

Authors

Charles Keweshan is a Senior Development Engineer who has been working in FCC product development since joining BASF in 1987. He has been a lead in development of bringing several FCC product platforms into commercial production including Reduxion, NaphthaMax, FlexTec, Unisphere and most recently Stamina. Previous to joining BASF, he worked for 10 years in Exxon's Corporate Research Science Lab in Annandale, NJ in the Carbonaceous Materials Characterization Group.

Daniel Neuman joined BASF as Senior Account Manager for FCC catalysts in 2007. He had developed considerable experience in FCC technology during earlier jobs with Mobil R&D Corp and with UOP-Katalistiks. Most recently, Dan worked in several management positions for TRICAT Industries Inc., mainly in the area of hydrotreating catalysts. Dan earned a BSChE and a Masters of Science in Chemical Engineering from Tufts University in Medford, MA. He is a member of Tau Beta Pi, the engineering honors society. Dan is the holder of several patents, and has authored many papers in the refining catalysts industry.

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